

# PATENT ABSTRACTS OF JAPAN

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(54) RESIN COMPOSITION FOR LASER MARKING, LASER MARKING METHOD AND LASER-MARKED MOLDED ARTICLE

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject composition capable of applying a clear white laser marking having high contrast by compounding a polyacetal resin with a carbon black having respectively specific DBP oil absorption and average particle diameter.

SOLUTION: The objective composition is produced by compounding (A) a polyacetal resin with (B) 0.001-1.0 wt.%, preferably 0.005-1.0 wt.%, more preferably 0.005-0.8 wt.% of a carbon black having a DBP oil, absorption of 70-200 mL/100 g, preferably 80-190 mL/100 g and an average particle diameter of 17-90 nm, preferably 18-50 nm and, as necessary, (C) conventional additives, fillers, other polymer materials, colorants, etc. The component B preferably has a coloring power to give a molded article having an L value of  $\leq 13.0$  when a composition produced by compounding the component A with 0.15 wt.% of the component B is injection-molded to form a plate having a thickness of 2 mm.

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## LEGAL STATUS

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## CLAIMS

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[Claim(s)]

[Claim 1] (a) It is (b) to polyacetal resin. The powdery carbon black whose DBP oil absorption is 70-200ml / 100g and whose mean particle diameter is 17-90nm is comparatively carried out in [ all ] a constituent, and it is 0.001-1.0. Resin constituent for laser marking characterized by doing weight % combination of.

[Claim 2] The resin constituent for laser marking according to claim 1 whose mean particle diameter of carbon black is 18-50nm.

[Claim 3] The resin constituent for laser marking according to claim 1 or 2 whose DBP oil absorption of carbon black is 80-190ml / 100g.

[Claim 4] The resin constituent for laser marking of claim 1-3 which is what has tinting strength from which L value of mold goods becomes 13.0 or less when carbon black blends this with polyacetal resin 0.15% of the weight and carries out injection molding to a plate with a thickness of 2mm given in any 1 term.

[Claim 5] Mold goods which consist of a resin constituent of claim 1-4 given in any 1 term (A) Or mold goods which irradiated and carried out laser marking of the laser light to the mold goods (A') covered with this resin constituent.

[Claim 6] Mold goods which irradiate laser light (A) Or mold goods according to claim 5 whose mold goods (A') are the mold goods which have 13.0 or less L value, and which were colored black substantially and which carried out laser marking.

[Claim 7] It hits irradiating laser at the mold goods covered with the mold goods or this resin constituent which consists of a polyacetal resin constituent, and performing marking, and is (a). It is (b) to polyacetal resin. The powdery carbon black whose DBP oil absorption is 70-200ml / 100g and whose mean particle diameter is 17-90nm or less is comparatively carried out in [ all ] a constituent, and it is 0.001-1.0. The laser marking approach characterized by using the resin constituent which comes to carry out weight % combination.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin constituent for laser marking suitably used in laser marking which gives the mark of a clear alphabetic character, a notation, etc. to the front face of the mold goods covered with resin mold goods or resin using laser light, the laser marking approach, and the mold goods which carried out laser marking.

[0002]

[Problem(s) to be Solved by the Invention] It considers as the approach of carrying out marking of an alphabetic character, a desired notation, or a desired pattern etc. to the front face of the mold goods covered for the purpose of giving discernment of a product, and design nature by resin mold goods or resin, and, generally printing in ink is performed from the former. However, since polyacetal was crystalline resin in printing, there was little ink with which can be satisfied of adhesion, and high printing of the adhesion force was in the condition next to impossible without pretreatment substantially in polyacetal. Depending on an operating environment, the problem that the damage resistance of the printing section in ink, abrasion resistance, and chemical resistance are not still more enough arises. Moreover, in printing in ink, there is a fault that a solvent and chlorofluocarbon need to be used because of resin surface washing, and it cannot be coped with to the trend of the world of solvent abolition in recent years or chlorofluocarbon washing abolition. As one means to solve such a problem, it is already proposed, the marking approach, i.e., laser marking, using laser light. As an approach of giving a desired mark by this laser marking, it is (1) at the beginning. Like physical change (for example, roughening of the front face in JP,58-67496,A etc.) of a laser-processing side Although the comparatively simple method of irradiating laser light on condition that a certain kind, and performing thermal processing was proposed Then, (2) Many methods of making laser marking nature discover positively with the device of the resin (for example, JP,63-216790,A, JP,61-41320,A, JP,1-306285,A) constituent of adding the bulking agent in which discoloration and decolorization are possible are reported. (2) Many of \*\*\*\*\* aim at performing vividly marking of a color which is different from the color of a base material from a demand of a commercial scene on the base material resin colored with the pigment etc. As part of laser marking to such a colored ingredient, there are many reports on a black system base material with a high demand in a commercial scene about the approach of obtaining a clear white mark. For example, although white marking is made possible by blending carbon black with plastics including polyacetal at JP,61-11771,B, the clearness of the marking section and the thing which cannot be referred to as sufficiently practical in respect of whiteness are almost the case. For example, although product discernment of a lot number etc. is possible, as a pattern as which design nature is required, it is not clear. Moreover, in JP,60-202119,A, marking nature is given by blending carbon black with an epoxy resin, and it is supposed that marking nature is improved, so that carbon black concentration increases. However, the same technique was applied to polyacetal resin, and the problem that marking nature tends to get worse also became clear, so that unlike the example of about [ that marking (white coloring) clear enough was not obtained only by blending the carbon black of arbitration ], and an epoxy resin carbon black concentration increased and the Japanese lacquer blackness of a base material improved. Moreover, according to JP,63-81117,A, marking nature is improved by making black titanium oxide contain in an epoxy resin, but especially when it applies to polyacetal similarly, in the polyacetal which carried out fiber strengthening, possibility that will cause breakage of fiber at the time of kneading of black titanium oxide and shaping, and a desired mechanical

property will be spoiled is large. Furthermore, although a kind of black pigment which changes from calcium phosphate and carbon to a thermoplastic polymer is made to contain and the improvement of marking nature is aimed at in JP,5-186633,A, in order to obtain desired Japanese lacquer blackness, the several to about 10 times amount of general carbon black is needed. Therefore, it is easy to generate gas at the time of about [ that there is a possibility of changing and worsening a property the outstanding mechanical property and over a long period of time / good / of the balance of polyacetal original ], and shaping, and the appearance of mold goods may be spoiled. From the above result, about white coloring marking to a black system base material, even if it applies the conventional technique to polyacetal resin, there is a trouble also in respect of marking nature or others. Therefore, the purpose of this invention is to offer the constituent and the laser marking approach contrast can give laser marking of a good and clear white system to the coloring base material which consists of polyacetal resin, especially a black system base material, without spoiling many outstanding properties which polyacetal resin has, and those balance.

[0003]

[Means for Solving the Problem] In order that this invention persons may attain the above-mentioned purpose, as a result of repeating research wholeheartedly, it resulted in a header and this invention that marking nature improved by leaps and bounds that there is close relation and by choosing these appropriately to the class and concentration, and marking nature of carbon black. That is, this invention is (a). It is (b) to polyacetal resin. The powdery carbon black whose DBP oil absorption is 70-200ml / 100g and whose mean particle diameter is 17-90nm is comparatively carried out in [ all ] a constituent, and it is 0.001-1.0. It is the laser marking approach characterized by using the resin constituent for laser marking characterized by carrying out, and this resin constituent weight % combination.

[0004]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. The polyacetal resin in this invention may be any of a homopolymer and a copolymer, and in the case of a copolymer, no matter the thing to which copolymerization of the monomer components, such as ethyleneoxide and dioxolane, was carried out at random for stabilization of a principal chain or a block, the thing by which graft polymerization was carried out, or the thing further introduced in the third component may be what copolymerization gestalt, it is not cared about.

[0005] Next, it sets to this invention and is the above (a). (b) blended with polyacetal resin Carbon black is explained. According to the place which this invention person examined, the coloring nature by the carbon black to the base material which generally consists of polyacetal resin especially the Japanese lacquer blackness in black coloring, and the laser marking nature to carbon black combination resin are greatly dependent on the loadings of carbon black at the structure and the list which are the mean particle diameter of the carbon black to blend, DBP oil absorption, i.e., the particle diameter which is carbon black particle independent magnitude, and the magnitude that the particle condensed. On the other hand, coloring nature, especially Japanese lacquer blackness and laser marking nature had the strong inclination which conflicts with the addition of carbon black, and selection of the carbon black for making good coloring nature and the outstanding laser marking nature coexist was very difficult. In this invention, in order to satisfy two engine performance in which solved the above difficult technical problems and it was thought that it conflicted to coincidence, the carbon black which controlled mean

particle diameter and structure highly, i.e., mean particle diameter, is 17-90nm, and it is characterized by using alternatively the carbon black whose DBP oil absorption is 70-200ml / 100g. When mean particle diameter is smaller than 17nm, the dispersibility of the carbon black to polyacetal resin worsens, and marking nature not only gets worse [ DBP oil absorption ], but [ 200ml / when larger than 100g ] it is inferior to productivity. Moreover, when mean particle diameter is larger than 90nm, DBP oil absorption 70ml / when smaller than 100g, too, marking nature gets worse and the quality and weatherability of coloring which are required of polyacetal resin at coincidence are inferior in it. Therefore, when coloring nature, laser marking nature, productivity, etc. are taken into consideration, the mean particle diameter of carbon black has desirable 17-90nm, and it is 18-50nm more preferably. Moreover, DBP oil absorption has a desirable thing (70-200ml / 100g), and they are 80-190ml / 100g more preferably. Moreover, what has specific tinting strength is desirable, and when carbon black is blended with polyacetal resin 0.15% of the weight and injection molding of this is carried out to a plate with a thickness of 2mm by the general process condition, specifically, what has tinting strength from which L value of mold goods becomes 13.0 or less is desirable [ the carbon black used for this invention ]. It is in charge of this evaluation, and what does not contain substantially the matter which checks coloring by carbon black as polyacetal resin is used. Although a detailed reason is not certain by using the carbon black which has the mean particle diameter and the DBP oil absorption property like the above, and has such tinting strength, compared with use of usual carbon black, laser marking nature improves remarkably, and it becomes possible to satisfy much more efficiently both coloring nature, especially Japanese lacquer blackness and laser marking nature. On the other hand, as it is in an example, there is a thing good as contrast also except the carbon black by this invention. However, the appearance of the marking section, i.e., the irregularity of the front face formed in the marking section and the non-marking section, is inferior to marking by this invention.

[0006] Being able to apply it, not only when combination of carbon black colors black but in case it tones this invention to other complicated colors further, when coloring it a gray color using a small amount of carbon black, using the carbon black of this invention for such an application gives a desirable result in laser marking nature. It carries out in [ all ] a constituent comparatively, and the concentration of the carbon black used for this invention from such a viewpoint is 0.001-1.0. It is weight % and this fully demonstrates the effectiveness. Carbon black concentration is 0.001. When smaller than weight %, the blackish color or gray color which can be used practically is not only hard to be obtained to polyacetal resin, but the effectiveness over marking by adding carbon black is not accepted. Furthermore, when it uses together with other coloring agents on the occasion of color coloring, it is hard to discover the effectiveness of the carbon black by this invention. On the other hand, little direction of the upper limit of carbon black concentration is good in the range which can color a base material a desired color. For example, it is 1.0 when coloring standard polyacetal resin black. It can color enough by the carbon black concentration with which weight % is not filled. However, there is the need of adding the carbon black of many in the purpose which raises the property of weatherability and others, plentifully. In this case, if the carbon black by this invention is used, carbon black concentration will be 1.0. Good laser marking can be performed securing the property of weatherability and others, if it is the range within weight %. However, it is carbon black 1.0 Even if it adds exceeding weight %, the Japanese lacquer blackness of a base material has a possibility that the stability of the mechanical

property of about [ not increasing more than this ] and constituent original or long-term physical properties may be spoiled. Furthermore, it has a bad influence on laser marking nature. such a thing -- taking into consideration -- the desirable loadings of carbon black -- 0.001-1.0 weight % -- more -- desirable -- 0.005-1.0 weight % -- especially -- desirable -- 0.005-0.8 It is weight %.

[0007] Moreover, in this invention, it is the range which does not spoil laser marking nature to the above-mentioned polyacetal resin constituent, and a well-known additive and/or a well-known bulking agent, and other polymeric materials can be added if needed in less than 70% of the weight of the range of parenchyma top all constituent weight. For example, it is the inorganic compound which made the subject various stabilizers, an antioxidant, lubricant, a nucleating additive, a plasticizer, a release agent, a lubricative grant agent, an antistatic agent, other polymeric materials or fibrous, a grain, the glass of powdered \*\*, the metal, and the metallic oxide.

[0008] In this invention, it is one of the suitable operation gestalten about this invention to perform marking of the white which was clear to the polyacetal resin by which the carbon black like the above was blended and black coloring was completely carried out on parenchyma, and excelled [ polyacetal resin ] in contrast. In this case, it consists of a polyacetal resin constituent with which carbon black was blended, and it is desirable to use the black coloring mold goods which have 13.0 or less L value as mold goods which irradiate laser light and should perform marking, and laser marking of it which was extremely excellent in contrast becomes possible.

[0009] Moreover, in this invention, coloring agents, such as a pigment and a color, can also be added further. That is, the carbon black by this invention raises not only white coloring but laser marking nature. If the carbon black by this invention is used together with other coloring agents in case it follows, for example, a base material is toned to a complicated color, a desirable result will be given in subsequent laser marking.

[0010] If it hits carrying out this invention, for there to be especially no limitation about the laser light source, the exposure approach, and equipments, and what is necessary is just well-known laser system. For example, well-known various kinds Nd; an YAG laser and CO2 Laser, various excimer lasers, etc. can use it suitably. Also in it, the effectiveness becomes remarkable in marking which used Nd; YAG laser.

[0011]

[Example] Hereafter, although an example explains this invention to a detail further, this invention is not limited to this.

The trial ingredient blended with examples 1-4, the example 1 of a comparison - 4 polyacetal resin at a rate which shows the following carbon black in Table 1 was prepared.

The following passes. Carbon black : The example 1:mean particle diameter of 18nm, the DBP oil absorption 130ml/100g example 2:mean particle diameter of 30nm, The DBP oil absorption of 113ml / 100g example 3 : The mean particle diameter of 42nm, The DBP oil absorption of 190ml / 100g example 4 : The mean particle diameter of 82nm, DBP oil absorption 71ml / example 1 of 100g comparison : [ Mean particle diameter of 24nm, ] DBP oil absorption 53ml / example 2 of 100g comparison : [ Mean particle diameter of 15nm, ] DBP oil absorption 65ml / example 3 of 100g comparison : [ Mean particle diameter of 18nm, ] DBP oil absorption 54ml / example 4 of 100g comparison: The mean particle diameter of 16nm, DBP oil absorption Injection molding of 55ml / the

100g above-mentioned resin ingredient was carried out, and the plate-like injection-molded product of 2mm in thickness, 50mm long, and 90mm wide was obtained. Laser marking was performed on condition that the following on these monotonous mold goods. The measurement of the contrast of the marking section of monotonous mold goods by which laser marking was carried out, and observation of the surface state of the marking section performed evaluation while it measured the Japanese lacquer blackness of monotonous mold goods by the following approach. An evaluation result is shown in Table 1 and drawing 1 -3.

[0012] [Laser marking conditions]

laser marking equipment: -- laser marker by NEC Corp. class [ of 475ESL2 laser ]: -- Nd; -- YAG laser (wavelength of 1064nm)

exposure method: -- power [ of the scanning formula (Q-switch frequency: 3kHz) marking section ]: -- 1 - 10W scan speed: 100 - 400 mm/S byte-size: -- 10-150 micrometers [the evaluation approach]

(Japanese lacquer blackness of monotonous mold goods) Color computer SM[ by Suga Test Instruments Co., Ltd. ]-4 mold was used, and L value was measured. Japanese lacquer blackness is so high that L value is small, and when it aims at black coloring, it is shown that coloring is good.

(Contrast of the marking section) Image processing system AT-100made from Micro Engineering U, and AreaSensor of the company The brightness of a blank and the brightness of the marking section which do not carry out marking were measured using the camera T-137, and it had the ratio (brightness of the brightness / marking section of a blank), and considered as the contrast value of the marking section. In this example, laser is irradiated and marking of a white system is given to the base material which blended carbon black and was colored the black system, and it means that good clear marking of contrast was obtained, so that the ratio of the brightness of a contrast value, i.e., the brightness / marking section of a blank, is large.

(Surface state of the marking section) Viewing and a feel estimated the surface state of the marking section in the four following steps.

- 4: The irregularity of the front face of the marking section is very small, and a feel is excellent.
- 3: The irregularity of the front face of the marking section is small, and a feel is good.
- 2: The irregularity of the front face of the marking section is somewhat large, and difficulty is in a feel.
- 1: The irregularity of the front face of the marking section is large, and a feel is bad. There is nonuniformity also in coloring.

When the carbon black specified in this invention is used so that clearly from Table 1 and drawing 1 -3, As opposed to marking of the contrast which was excellent in the range large irrespective of change of carbon black concentration, and a surface state being attained When the carbon black except this invention prescribing is used, carbon black serves as marking which is inferior in a surface state in a low concentration field ( drawing 1 ). Conversely, in a height concentration field ( drawing 3 ), it is difficult carbon black for it to be stabilized and to obtain marking with which it becomes marking in which contrast is inferior, and is satisfied of both [ both ] contrast and surface state.

[0013]

[Table 1]

	カーボンブラック		カーボン濃度 (重量%)	L 値	コントラスト値	マーク部の 表面状態 (目視)
	平均粒子径 (nm)	DBP 吸油量 (ml/100g)				
実施例 1	18	130	0.05	13.0	9.9	4
			0.15	12.5	9.5	4
			0.25	12.5	7.9	4
実施例 2	30	113	0.05	15.3	10.0	3
			0.15	12.4	9.2	4
			0.25	12.3	8.5	4
実施例 3	42	190	0.05	15.4	9.6	4
			0.15	12.7	8.4	4
			0.25	12.4	8.6	4
実施例 4	82	71	0.05	13.9	9.8	3
			0.15	12.9	8.5	4
			0.25	12.8	7.3	4
比較例 1	24	53	0.05	14.2	10.0	1
			0.15	12.4	7.9	2
			0.25	12.2	5.0	4
比較例 2	15	65	0.05	14.5	9.5	1
			0.15	12.3	7.8	3
			0.25	12.2	5.1	4
比較例 3	18	54	0.05	14.3	10.0	1
			0.15	12.4	7.2	3
			0.25	12.3	4.8	4
比較例 4	16	55	0.05	15.0	9.3	2
			0.15	12.1	7.2	3
			0.25	12.1	6.0	4

DESCRIPTION OF DRAWINGS



[Brief Description of the Drawings]

[Drawing 1] In the example and the example of a comparison of this application, it is the graph which shows relation with the surface state and contrast by the used carbon black (0.05 % of the weight of carbon black concentration).

[Drawing 2] In the example and the example of a comparison of this application, it is the graph which shows relation with the surface state and contrast by the used carbon black (0.15 % of the weight of carbon black concentration).

[Drawing 3] In the example and the example of a comparison of this application, it is the graph which shows relation with the surface state and contrast by the used carbon black (0.25 % of the weight of carbon black concentration).

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[Translation done.]

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Age Group	Number of Subjects
18-24	10
25-34	20
35-44	30
45-54	40
55-64	50
65-74	60
75+	100

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Figure 1 is a line graph showing the percentage of respondents who believe that the use of force is justified in various circumstances. The x-axis represents the percentage of respondents who believe that the use of force is justified in the circumstances, ranging from 0% to 100%. The y-axis represents the percentage of respondents who believe that the use of force is justified in the circumstances, ranging from 0% to 100%. The graph shows a general trend of increasing justification for the use of force as the percentage of respondents who believe that the use of force is justified in the circumstances increases.

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